

# Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions

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[1] We present a novel capability in satellite remote sensing with implications for air pollution control strategy. We show that the ratio of formaldehyde columns to tropospheric nitrogen dioxide columns is an indicator of the relative sensitivity of surface ozone to emissions of nitrogen oxides ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) and volatile organic compounds (VOCs). The diagnosis from these space-based observations is highly consistent with current understanding of surface ozone chemistry based on in situ observations. The satellite-derived ratios indicate that surface ozone is more sensitive to emissions of  $\text{NO}_x$  than of VOCs throughout most continental regions of the Northern Hemisphere during summer. Exceptions include Los Angeles and industrial areas of Germany. A seasonal transition occurs in the fall when surface ozone becomes less sensitive to  $\text{NO}_x$  and more sensitive to VOCs.

**INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques. **Citation:** Martin, R. V., A. M. Fiore, and A. Van Donkelaar (2004), Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions, *Geophys. Res. Lett.*, **31**, L06120, doi:10.1029/2004GL019416.

## 1. Introduction

[2] Surface ozone is deleterious to human health, crops, and ecosystems [National Research Council, 1991]. Uncertainty in the relation between surface ozone and its two main precursors, nitrogen oxides ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) and volatile organic compounds (VOCs) remains a primary obstacle to improving surface air quality [Sillman, 1999]. Ozone is produced in both  $\text{NO}_x$ -sensitive and  $\text{NO}_x$ -saturated (also known as VOC-sensitive) regimes. The design of control strategies for surface ozone has been impeded by limited observations of ozone- $\text{NO}_x$ -VOC sensitivity [Sillman, 1999]. We develop a method to use space-based observations from the Global Ozone Monitoring Experiment (GOME) [European Space Agency, 1995; Burrows *et al.*, 1999] to characterize ozone- $\text{NO}_x$ -VOC sensitivity in

surface air and apply our method to determine the spatial and temporal variation in ozone- $\text{NO}_x$ -VOC sensitivity throughout the Northern Hemisphere.

[3] Surface ozone is produced by a chain reaction involving the photochemical oxidation of VOCs in the presence of  $\text{NO}_x$ . The chain reaction is propagated by cycling of  $\text{HO}_x$  ( $\equiv \text{OH} + \text{peroxy}$ ) radicals. The pathway for  $\text{HO}_x$  loss is determined by the relative abundance of  $\text{HO}_x$  and  $\text{NO}_x$ . Ozone production tends to be either  $\text{NO}_x$ -sensitive if  $\text{HO}_x$ -loss occurs primarily by self reaction of peroxy radicals, or  $\text{NO}_x$ -saturated if the primary  $\text{HO}_x$ -loss pathway is via reaction of nitrogen dioxide ( $\text{NO}_2$ ) and OH [Sillman *et al.*, 1990]. Sillman [1995] first presented the concept of using ozone- $\text{NO}_x$ -VOC indicators to diagnose  $\text{NO}_x$ -sensitive versus  $\text{NO}_x$ -saturated conditions, and showed that the ratio of formaldehyde (HCHO) to total reactive nitrogen is such an indicator. A related ratio can be retrieved from the GOME satellite instrument, specifically the ratio of the HCHO column to the tropospheric  $\text{NO}_2$  column.

## 2. Evaluation of the HCHO/ $\text{NO}_2$ Column Ratio as an Ozone- $\text{NO}_x$ -VOC Indicator

[4] We use the GEOS-CHEM global 3-D model of ozone- $\text{NO}_x$ -VOC chemistry [Bey *et al.*, 2001], version 4.16 [Martin *et al.*, 2002a], to evaluate the quality of the HCHO/ $\text{NO}_2$  column ratio as an indicator of  $\text{NO}_x$ -sensitive versus  $\text{NO}_x$ -saturated conditions. We analyze results from three simulations previously described by Fiore *et al.* [2002]: a standard simulation, a simulation in which anthropogenic VOC emissions are reduced by 50%, and a simulation in which anthropogenic  $\text{NO}_x$  emissions are reduced by 50%. The simulations use assimilated observations of meteorological fields from NASA GEOS-1 with 20 vertical levels and a  $4^\circ \times 5^\circ$  horizontal resolution. All simulations are spun up for 10 months to remove the effects of initial conditions. We present results for May–November.

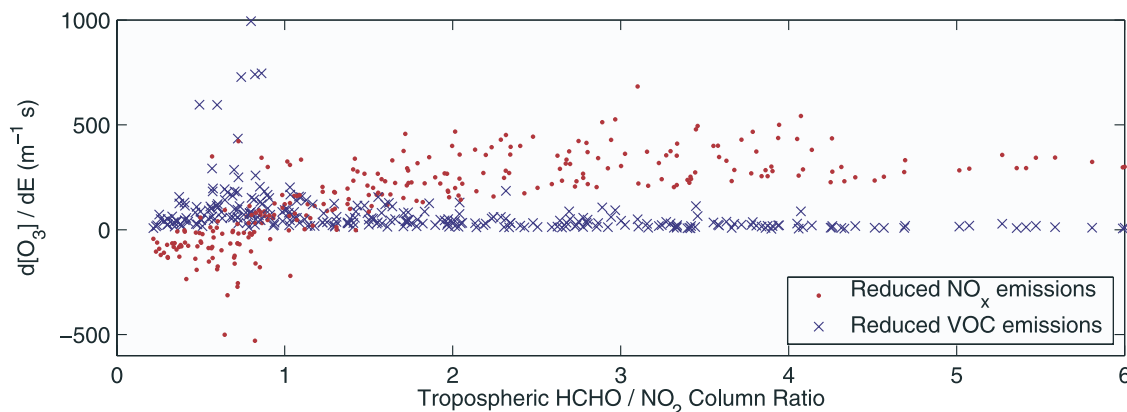
[5] Figure 1 shows the calculated response in monthly-mean afternoon surface ozone over polluted regions to a prescribed change in emissions as a function of the tropospheric HCHO/ $\text{NO}_2$  column ratio. The transition between  $\text{NO}_x$ -sensitive and  $\text{NO}_x$ -saturated regimes occurs for a HCHO/ $\text{NO}_2$  ratio of about 1. HCHO/ $\text{NO}_2$  ratios above 1 tend to be  $\text{NO}_x$ -sensitive as indicated by the decrease in surface ozone for the simulation with reduced  $\text{NO}_x$  emissions. HCHO/ $\text{NO}_2$  ratios below 1 reflect  $\text{NO}_x$ -saturated conditions; reductions in  $\text{NO}_x$  emissions increase surface ozone while reductions in VOC emissions decrease surface ozone.

[6] Why does the HCHO/ $\text{NO}_2$  column ratio function effectively as an indicator of surface ozone- $\text{NO}_x$ -VOC sensitivity? First, the bulk of the tropospheric  $\text{NO}_2$  and

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**Figure 1.** Model calculation of the normalized local sensitivity of afternoon surface ozone,  $d[O_3]/dE$ , to a 50% reduction in anthropogenic emissions,  $dE$ , in units of either molecules nitrogen  $m^{-2} s^{-1}$  or molecules carbon  $m^{-2} s^{-1}$ . The local sensitivity and local model tropospheric HCHO/NO<sub>2</sub> column ratio are monthly mean values from May to November. Afternoon surface ozone is the average between 1 pm and 5 pm local time. The calculation is restricted to polluted regions (model tropospheric NO<sub>2</sub> column  $>2.5 \times 10^{15}$  molecules  $cm^{-2}$ ).

HCHO columns over polluted regions is within the mixed layer [Ladstätter-Weissenmayer *et al.*, 2003]. Second, the division between NO<sub>x</sub>-sensitive and NO<sub>x</sub>-saturated regimes generally follows a constant reactivity-weighted VOC/NO<sub>x</sub> ratio [Chameides *et al.*, 1992], a ratio closely associated to the HCHO/NO<sub>2</sub> ratio. Third, the HCHO/NO<sub>2</sub> column ratio largely reflects the ratio of HO<sub>x</sub> to NO<sub>x</sub> sources near the surface. HCHO is positively correlated with the source of HO<sub>x</sub> in polluted environments [Martinez *et al.*, 2003], and tropospheric NO<sub>2</sub> is closely related to NO<sub>x</sub> emissions [Leue *et al.*, 2001; Martin *et al.*, 2003]. The ratio of the HO<sub>x</sub> source to the NO<sub>x</sub> source determines NO<sub>x</sub>-VOC sensitivity, and the transition from NO<sub>x</sub>-sensitive to NO<sub>x</sub>-saturated regimes occurs at a specific ratio over a range of conditions [Kleinman, 1991; Jacob *et al.*, 1995].

### 3. Space-Based Observations of Tropospheric NO<sub>2</sub> and HCHO

[7] The nadir-viewing GOME satellite instrument has provided the capability for continuous global monitoring of tropospheric NO<sub>2</sub> and HCHO columns through observation of solar backscatter since 1995. Global coverage is achieved every 3 days after 43 orbits with a typical surface spatial resolution of 40 km by 320 km, sufficient to resolve the regional scale of ozone pollution episodes [Logan, 1989]. Observations at northern mid-latitudes occur between 10:30 AM–11:30 AM local solar time. Our numerical model calculations show that the HCHO/NO<sub>2</sub> ratio exhibits little diurnal variation during daytime; the ratio at 11 AM is typically within 5% of the ratio in the afternoon, so the thresholds identified in Figure 1 are applicable to GOME observations.

[8] The GOME retrievals are described in Martin *et al.* [2002b, 2003] for tropospheric NO<sub>2</sub> and in Chance *et al.* [2000] and Abbot *et al.* [2003] for HCHO. These retrievals include the air mass factor (AMF) formulation of Palmer *et al.* [2001] and radiative transfer calculations with the Linearized Discrete Ordinate Radiative Transfer (LIDORT) model developed by Spurr [2002]. Observation scenes are

excluded when local cloud cover retrieved from GOME [Kurosu *et al.*, 1999] exceeds 40%.

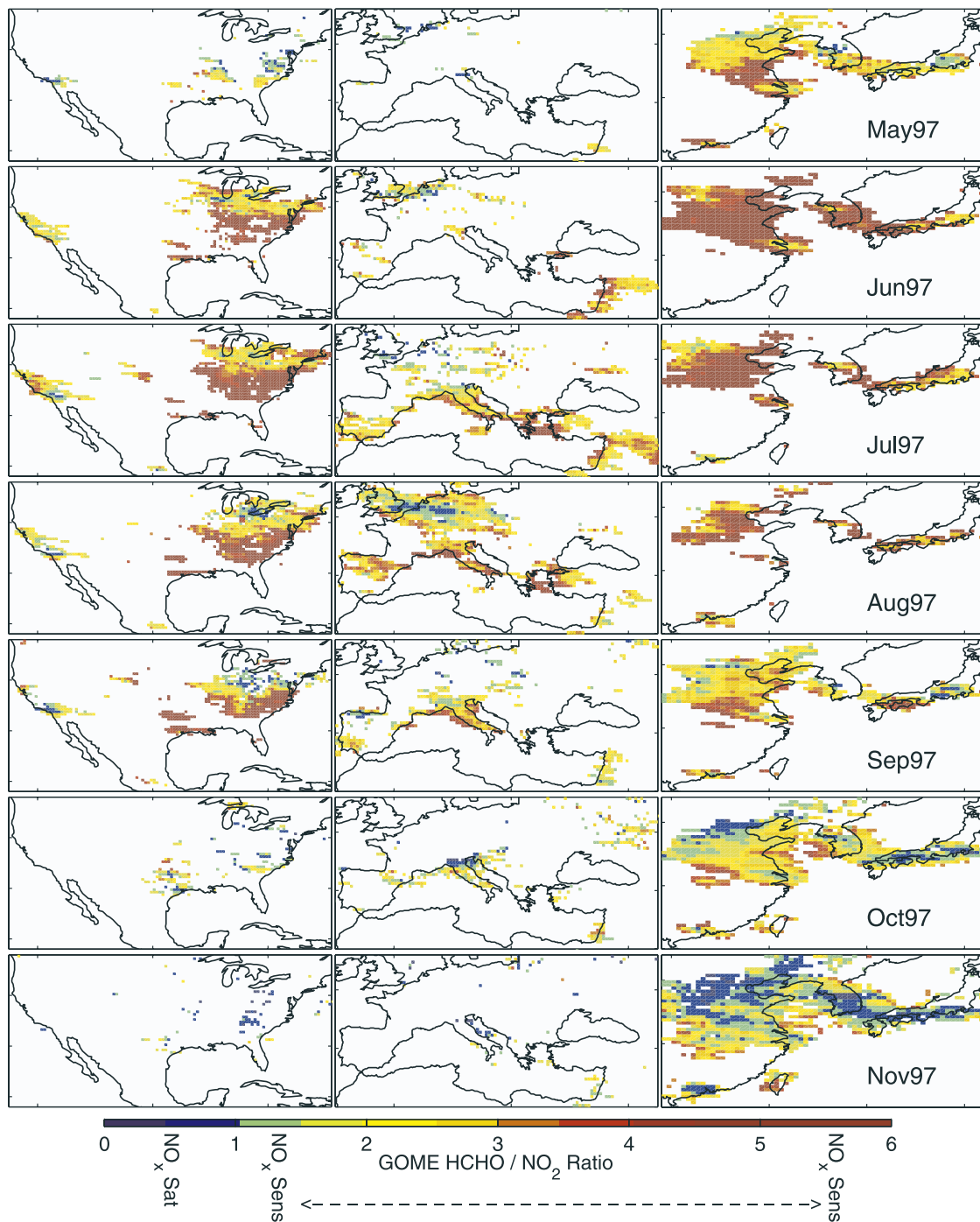
[9] Errors in the GOME HCHO/NO<sub>2</sub> ratio are reduced by compensating effects. The largest source of error in individual trace gas retrievals is from the AMF calculation due to surface reflectivity, clouds, aerosols, and trace gas profile [Martin *et al.*, 2002b; Boersma *et al.*, 2004]. Error in the AMF calculation similarly affects NO<sub>2</sub> and HCHO retrievals and largely cancels in the ratio. Uncertainty in the resulting monthly mean ratio is typically less than 25%.

### 4. Ozone-NO<sub>x</sub>-VOC Sensitivity Diagnosed From Space-Based Observations

[10] Figure 2 shows the GOME HCHO/NO<sub>2</sub> column ratio over North America, Europe, and East Asia during May to November 1997. Ratios greater than one, indicating NO<sub>x</sub>-sensitive conditions over most suburban and rural areas during summer, are consistent with analysis of in situ observations at rural sites of North America by Trainer *et al.* [1993]. The decrease in the HCHO/NO<sub>2</sub> ratio to less than one over the eastern United States during fall shows the seasonal transition from NO<sub>x</sub>-sensitive to NO<sub>x</sub>-saturated conditions due to a decline in isoprene and HO<sub>x</sub> that is expected from theory [Kleinman, 1991], in situ [Jacob *et al.*, 1995], and models [Liang *et al.*, 1998]. The seasonal decline in isoprene and HO<sub>x</sub> is also associated with a seasonal decline in the HCHO column to values below the GOME detection limit.

[11] GOME shows that major urban and industrial centers such as Los Angeles tend to be NO<sub>x</sub>-saturated, but transition to a NO<sub>x</sub>-sensitive regime downwind, consistent with model calculations by Milford *et al.* [1989]. The initial NO<sub>x</sub> supply greatly exceeds the HO<sub>x</sub> supply in major urban areas, but a switch from NO<sub>x</sub>-saturated to NO<sub>x</sub>-sensitive conditions occurs from the combined effects of dilution and HO<sub>x</sub> production downwind, as the HO<sub>x</sub> supply surpasses the initial NO<sub>x</sub> source [Kleinman, 1991, 1994].

[12] Data over Europe are sparse due to HCHO columns below the GOME detection limit. London is near NO<sub>x</sub>-saturation, consistent with calculations of Derwent *et al.*



**Figure 2.** Monthly mean tropospheric HCHO/NO<sub>2</sub> column ratio retrieved from the GOME satellite instrument for North America, Europe, and East Asia. Ratios greater than 1 tend to be NO<sub>x</sub>-sensitive. Ratios below 1 tend to be NO<sub>x</sub>-saturated. White areas indicate remote regions (observed tropospheric NO<sub>2</sub> columns less than  $2.5 \times 10^{15}$  molecules cm<sup>-2</sup>) and regions below the HCHO detection limit of  $4 \times 10^{15}$  molecules cm<sup>-2</sup>.

[2003]. In situ measurements [Staffelbach *et al.*, 1997] support GOME observations that southern Switzerland is NO<sub>x</sub>-sensitive during summer. GOME reveals that industrial Germany is NO<sub>x</sub>-saturated throughout the year, and that a transition from NO<sub>x</sub>-sensitive to NO<sub>x</sub>-saturated conditions occurs over the Po Valley from September to October.

[13] GOME HCHO/NO<sub>2</sub> ratios greater than one during summer over eastern China, Korea, and Japan indicate NO<sub>x</sub>-

sensitive conditions. However, there is a clear transition to NO<sub>x</sub>-saturated conditions in the northern regions during fall. The resulting gradient during October and November of NO<sub>x</sub>-sensitive conditions in rural southern China, but NO<sub>x</sub>-saturated conditions elsewhere, is consistent with photochemical model calculations of Luo *et al.* [2000]. This transition is of particular interest since episodes of enhanced ozone concentrations are frequent in the fall, and may be reducing crop yields [Chameides *et al.*, 1999].



[14] Results presented here suggest that nascent capabilities in satellite remote sensing are of sufficient quality to contribute to air pollution management by providing guidance on the spatial and temporal sensitivity of surface ozone to reductions of  $\text{NO}_x$  and VOC emissions. Such observations also provide a critical test of air quality models used to develop emission controls. These observational capabilities will be enhanced by the next generation of instruments, such as the SCIAMACHY and OMI satellite instruments, which feature higher spatial resolution that should resolve transitions between urban and suburban environments. Future work should systematically examine the relationship of these space-based column indicators with high-resolution simulations and in situ indicators.

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